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### Radiative recombination processes of thermal donors in silicon

S. Pizzini, S. Binetti, E. Leoni, A. Le Donne, M. Acciarri, A. Castaldini(\*)

INFN and Department of Materials Science, University Milano-Bicocca, Via Cozzi 53, Milano, Italy

(\*)INFN and Department of Physics, University of Bologna, Viale Berti Pichat 6/2, Bologna, Italy

#### ABSTRACT

There is a recent, renewed attention on the possible development of optical emitters compatible with silicon microelectronic technology and it has been recently shown that light emitting diodes could be manufactured on dislocated silicon, where dislocations were generated by plastic deformation or ion implantation. Among other potential sources of room temperature light emission, compatible with standard silicon-based ULSI technology, we have studied old thermal donors (OTD), as the origin of their luminescence is still matter of controversy and demands further investigation.

In this work we discuss the results of a spectroscopical study of OTD using photoluminescence (PL) and Deep Level Transient Spectroscopy (DLTS) on standard Czochralsky (Cz) silicon samples and on carbon-doped samples.

We were able to show that their main optical activity, which consists of a narrow band at 0.767 eV (P line), is correlated to a transition from a shallow donor level of OTD to a deep level at  $E_v+0.37$  eV which is tentatively associated to C-O complexes. As we have shown that the P line emission persists at room temperature, we discuss about its potentialities to silicon in optoelectronic applications.

#### INTRODUCTION

It is well known that a long dwelling at temperatures around 450°C during the cooling cycle of large diameter, crucible grown, oxygen-rich Cz silicon or any thermal annealing of Cz silicon in the same temperatures range, leads to the generation of oxygen related donors, often referred as Old Thermal Donors (OTD), to distinguish them from other types of thermal donors that can be formed in the temperature range 600–700 °C and today known as New Thermal Donors (NTD). Since their discovery generations of investigators addressed their studies to the microscopic structure, the growth and decomposition kinetics as well as the electrical and optical properties of OTDs, using all the techniques suitable for the study of electrically and optically active, paramagnetic centres.

In spite of many thousands (around 19000) of papers published on the topic, which make of the OTDs one of the most studied defect centres in semiconductors, and whose properties have been recently reviewed by Newman [1] a defect model which consistently explains all their features, including their optical properties, is still lacking.

In fact, while it is well known that oxygen rich silicon annealed at 450 °C for several hours exhibits a prominent photoluminescence spectrum with a narrow no-phonon line at 0.767 eV, generally labelled P line [2], a direct proof that oxygen is incorporated in the centre has not yet been given. Furthermore, PL measurements have cast doubts on a simple relationship between thermal donors and the P line [3]. Eventually, a carbon isotopic effect experimentally determined in the P line shows a possible involvement of carbon-oxygen complexes in the defect involved in the P line luminescence [2].

In this work we will present and discuss the results of a systematic study of the photoluminescence properties of old thermal donors, carried out on carbon-lean and carbon-doped Cz samples, with the aim looking to possible applications of the P-line in optoelectronic applications.

## EXPERIMENTAL

In the experiments the following samples were examined:

- (1) n-type ( $\rho = 3.5\text{--}5\text{ Ohm cm}$ ) (100) Cz silicon samples with oxygen concentration of 18 ppma, carbon content below the FTIR detection limits ( $<0.1\text{ ppma}$ ) (kindly supplied by MEMC Electronic Materials, Italy). These samples are designed as CzM.
- (2) n-type ( $\rho = 18\text{--}15\text{ Ohm cm}$ ) (100) Czochralski grown silicon doped with carbon during the growth process (kindly supplied by Institute for Material Science Research of Sendai, Japan)  $[O] = 24\text{ ppma}$ ,  $[C] = 1\text{ ppma}$ . These samples are designed as CzJ.

The samples were treated for times variable from 8 to 100 hours at  $470^\circ\text{C}$  in order to induce the thermal donors generation, while their dissolution has been achieved by thermal treatment at  $650^\circ\text{C}$  for 10'. Prior to thermal treatments, the samples were CP4 and RCA etched and then were closed under vacuum in quartz ampoules. The oxygen losses resulting from the annealing are deduced from room temperature FTIR measurements. The resistivity of all the samples, before and after any thermal treatments has been measured for OTD concentration determination according the ASTM procedure F 723-88. The values of diffusion length of minority carriers were measured by the Surface Photovoltage technique. Details are reported in [4]. The photoluminescence (PL) spectra of both sets of samples were recorded with a spectral resolution of 6 nm ( $\Delta E = 4\text{ meV}$ ), using standard lock-in techniques in conjunction with a grating monochromator and InGaAs as a detector. For the excitation, a quantum well laser ( $\lambda = 808\text{ nm}$ ) was used. The measurements were performed in the temperature range 12–300 K. Standard DLTS measurements have been performed by means of a SULA Tech. Inc. instrumentation. The temperature has been varied from the liquid nitrogen temperature to 350 K with reverse bias ranging from -4V to 0 and a pulse width from 1 to 10ms.

Minority carrier traps have been detected by minority carrier transient spectroscopy (MCTS). MCTS is a technique that measures the capture and emission of minority carriers at deep states within the band gap. In this technique injection of carriers is by a light pulse of above-band-gap radiation incident on a semitransparent Schottky diode. During the measurement the controlling excess carrier species are minority carriers, generated behind the depletion region by optical excitation while the sample is held under reverse bias. The electric field in the depletion region excludes majority carriers. Photogenerated minority carriers created within a diffusion length from the depletion region may then enter the depletion region and be available for capture. Schottky diode under test is maintained at a constant value of applied reverse bias, in our case 4V.

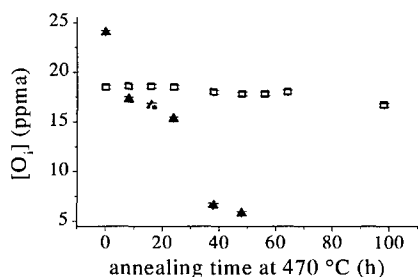
## RESULTS

### CzM samples

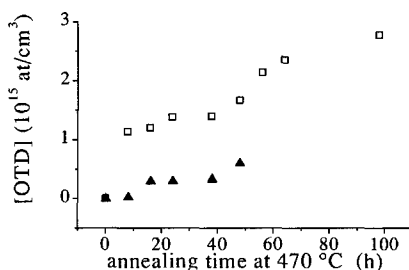
The effect of annealing time at  $470^\circ\text{C}$  on the concentration of interstitial oxygen  $[O_i]$ , and of OTDs is displayed in Figs. 1 and 2 while the time evolution of the diffusion length is reported in Fig.3.

As it is expected from earlier literature data, the concentration of OTDs increases almost linearly with the annealing time. Moreover, this increase is associated to a decrease of the diffusion length (see Fig.3), which saturates after about 20 hr. The photoluminescence spectra of these samples, collected after different annealing times at 470°C, present common features, as it is shown in Fig. 4, which reports a typical spectrum. In fact, a very intense P line is always present, together with two weak signals known in literature [2,5] as the C line at 0.789 eV and the H line at 0.925 eV and the band edge luminescence at 1.1 eV.

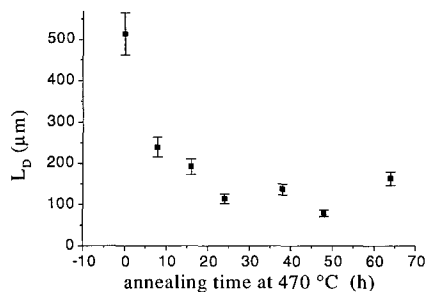
While the energy position of the P line has been verified to remain unaltered at increasing annealing times and by increasing the laser power within four orders of magnitude (from 0.02 mW to 60 mW), its intensity shows a typical trend, with the duration of the heat treatment.



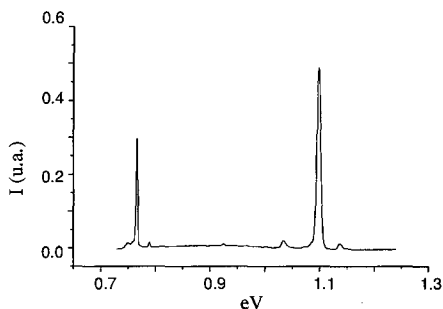
**Figure 1.** Evolution of the concentration of the interstitial oxygen with the annealing time at 470°C (□ CzM sample, ▲ CzJ sample).



**Figure 2.** Evolution of the OTD concentration with the annealing time at 470°C (□ CzM sample, ▲ CzJ sample).



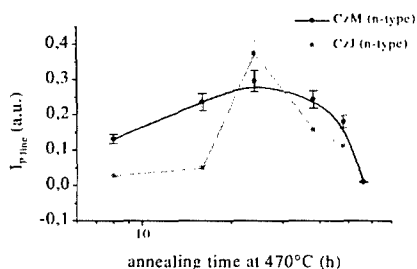
**Figure 3.** Evolution of diffusion length of minority carriers with the annealing time at 470 °C in the CzM sample.



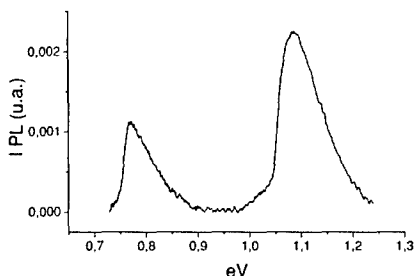
**Figure 4.** PL spectrum of a CzM sample after an annealing at 470 °C for 24 h ( $T=12$  K,  $P = 6\text{W}/\text{cm}^2$ ,  $\Delta E=4$  meV ).

The intensity of the P line, increases, in fact, up to a maximum after about 25 hr, and then decreases for thermal treatments of longer duration, as shown in Fig.5

It is worth to remark that this behaviour is largely uncorrelated with the total concentration of OTDs, which increases steadily (see Fig. 2), but follows almost exactly the behaviour of the PL intensity of the OTD-bound exciton emission in the TO region and the concentration of the NL8 donor, which both peak in fact at about 20 hours, as reported by Liesert et. [6] and Newman [1]. It is rather interesting, and never cited in literature, that the decrease of the diffusion length with the annealing time saturates in correspondence of the maximum of the P-line intensity, indicating a common trend with density of recombination centres and the intensity of the P-line. It is important to note that the intensities of the C and H lines remain instead constant with the entire duration of the heat treatment.

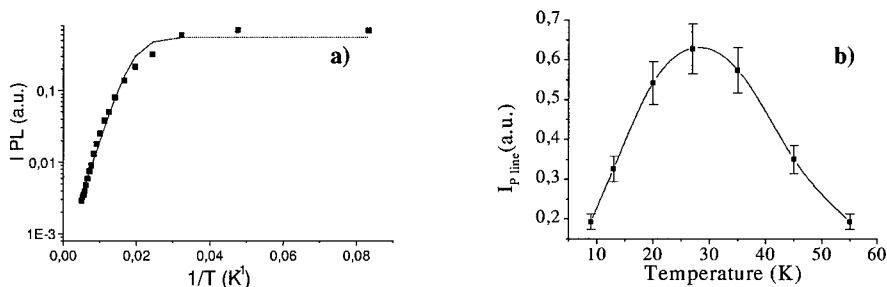


**Figure 5.** Evolution of the intensity of the P line with the annealing time at 470 °C (● CzM sample, ○ CzJ sample). The curves through the points are a guide for the eyes.



**Figure 6.** Typical photoluminescence spectrum of OTDs at room temperature ( $P=6\text{W/cm}^2$ ,  $\Delta E=4\text{ meV}$ ).

The P line signal persists up to room temperature with a substantial decrease in intensity and an almost constant ratio with the band edge luminescence, as it is shown in Fig. 6. The thermal quenching occurs at temperatures above 50 K with a thermal dissociation energy of 31 meV (see Fig. 7.a). An increase of the P line intensity is observed between 12 and 30 K (see Fig. 7.b), in agreement to previous results of Davies [7] who explains this behaviour as a result of competition between the optical centres and other (shallow) traps. With increasing temperature the excitons freed from the traps become available for capture by photoluminescence centres. Table I displays the DLTS and MCTS results where only the traps present after the thermal treatment for 24 h and 64 h are reported. From this table we can observe the set-up of a shallow level at  $E_c-0.015\text{ eV}$  (related to thermal donors) after 24 hr, which permains after 64 h as well as two deep levels at  $E_c-0.33$  and  $E_c-0.34$  of which one sets up after 64 h. From MCTS measurements a trap at  $E_v+0.37\text{ eV}$  has been detected, which falls very close to the energy of the trap observed by with Hall effect measurements [10] in similarly prepared samples.



**Figure 7** a) Thermal quenching of the P line b) Temperature dependence of the P line in 10-60 K range.

| Samples<br>TT 470°C | $E_c - E$ [eV] | $\sigma$ [cm <sup>2</sup> ] | $N_T$<br>[cm <sup>-3</sup> ] | Remarks |
|---------------------|----------------|-----------------------------|------------------------------|---------|
| 24h                 | 0.014          | $4.3 \times 10^{-21}$       | $9.2 \times 10^{11}$         | DLTS    |
|                     | 0.33           | $2.5 \times 10^{-16}$       |                              |         |
| 64h                 | 0.015          | $1.7 \times 10^{-20}$       | $8.7 \times 10^{11}$         | DLTS    |
|                     | 0.34           | $6.2 \times 10^{-17}$       | $1.2 \times 10^{12}$         |         |
|                     | 0.33           | $2.3 \times 10^{-18}$       |                              |         |
| Samples<br>TT 470°C | $E_v + E$ [eV] | $\sigma$ [cm <sup>2</sup> ] |                              | Remarks |
| 24h                 | 0.37           | $1.75 \times 10^{-18}$      |                              | MCTS    |

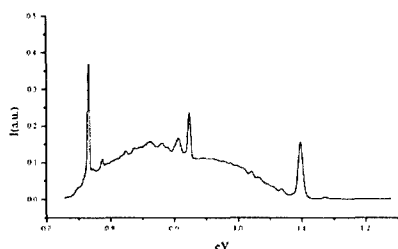
**Table I** Summary of the properties of the majority and minority carrier traps found by DLTS and MCTS.

### CzI samples

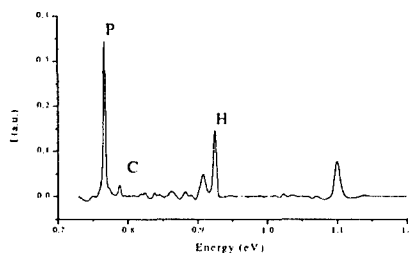
As it could be observed in Figs. 1 and 2 the effect of annealing on  $[O_i]$ , and OTD concentration is quite different with respect to the CzM samples. In fact, while in the former samples the oxygen concentration remains almost constant (its decrease is of the order of the donor formed, i.e. less than 1% of the initial oxygen concentration) with the annealing time, in these samples the oxygen concentration decreases down to 5 ppma, as the carbon concentration does, going below the detection limit. This can be easily explained by considering that the presence of carbon favours the oxygen precipitation as oxide. In fact, oxygen *per se* requires an excess volume to segregate as an oxide, which must be normally delivered either by vacancy absorption or self-interstitial emission. As carbon precipitation is as well volume exigent, its molar volume being half of the silicon matrix, the simultaneous presence of both oxygen and carbon favours [8] their co-precipitation.

It should be however remarked that the concentration of carbon in these samples is only little in excess over that present in former samples, indicating either a strong catalytic effect or some effect associated to an excess of IR-inactive carbon content in the oxygen segregation processes. Another striking difference is the total amount of donors formed, which is always in defect with respect to than found in CzM samples, as an indication that the overall kinetics of OTD formation is influenced by the simultaneous occurring of the oxygen segregation.

The presence of carbon has also a striking effect on the features of PL spectra, as it is shown in Fig.8. The presence of a broad band within 0.7 and 1.0 eV is clearly evident, on which the P, C and H lines [2,5] are superimposed, together with a multiplicity of other emissions of minor intensity and a strong band edge emission, which are better evidenced while removing the broad band contribution to the background, as it is shown in Fig. 9.



**Figure 8.** PL spectrum of CzJ heat treated at 470°C for 24h ( $T=12\text{ K}$ ,  $P=6\text{ W/cm}^2$ ,  $\Delta E = 4\text{ meV}$ ).



**Figure 9.** PL spectra of sample CzJ TT 470 °C 24 h after background subtraction.

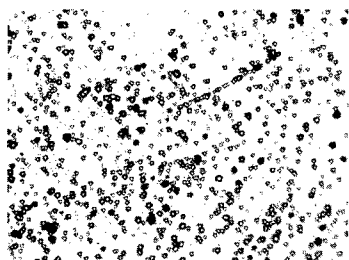
Incidentally, a broad band in the same energy range was found as the unique PL fingerprint of the segregation of oxide nanoparticles in Cz samples annealed at 650°C for 64h [9].

It should be also remarked that the PL intensity of the P line is quite comparable with that observed in carbon-lean samples, in spite of the lesser density of donors formed and a larger integral radiative emission of the sample.

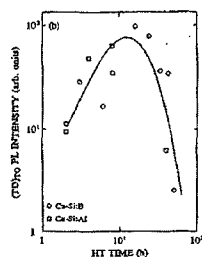
The difference between the spectral features of the PL in CzM and CzJ samples can be associated to the segregation of carbon and oxygen, which can be in fact monitored by optical microscopy after Schimmel etching (see Fig. 10). The presence of precipitates together with dislocations, where the last do however not manifest their presence in the PL spectra, is clearly evident from the triangular etch pits.

As in the case of the CzM samples, the P line disappears after a thermal dissolution treatment at 650 °C.

The evolution of the intensity of the P line in CzJ with the annealing time is reported in Fig. 5, which shows a substantial agreement with the behaviour of carbon-lean samples, both in the peak energy and in the maximum absolute intensities.



**Figure 10.** Optical micrograph of Schimmel etched sample CzJ TT for 24 h at 470 °C (x 1000).



**Figure 11.** Annealing-time dependence of the OTD-bound exciton emission band intensity in the TO region for various boron and aluminium doped silicon crystal.

## DISCUSSION

The interest of the present results is twofold, concerning both the physics of the light emission from OTD and the potentialities of the OTDs as room temperature light emitting centres. About the first issue, some main key points come from this work. At first, a shallow donor level at  $E_c - 0.014$  eV and a deep level at  $E_v + 0.37$  eV were detected by DLTS and MCTS measurements, where the second falls very close to the energy of the trap observed by with Hall effect measurements [10] in similarly prepared samples. The annealing time dependence of the P line luminescence follows the corresponding evolution of the NL8 donor and of the OTD-bound exciton (see Fig. 11) observed by Liesert et al. [6]. If we consider that the P-line emission correspond to a radiative transition between a donor level at  $E_c - 0.0015$  eV and the deep trap at  $E_v + 0.37$  eV we could fit within few meV the P line emission energy at 0.767 eV, and conclude that the P luminescence originates from a transition from a OTD level to a deep level corresponding to a C-O complexes, as already proposed by some of us in a former article [3]. About the second issue, we have demonstrated that OTDs emit light at room temperature, although with a hundredfold decrease of intensity with respect to cryogenic temperatures. The comparable values of the thermal dissociation energy (31 meV) and the energy of the shallow level which sets-up with the annealing at 470°C and which is involved in the P-line transition, calls for a quenching mechanism associated to the thermal donor ionisation. It seems therefore restricted by the physics of the PL luminescence processes of OTDs in carbon-lean samples and by the presence of non-radiative recombination centres in carbon-doped samples any possible further increase of the PL of OTDs.

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